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Journal

Journal of Geophysical Research Atmospheres, 104(D17)

ISSN

0148-0227

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Publication Date

1999-09-20

DOI

10.1029/1999JD900238

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Aircraft measurements of the latitudinal, vertical, and seasonal variations of NMHCs, methyl nitrate, methyl halides, and DMS during the First Aerosol Characterization Experiment (ACE 1)

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Abstract. Canister sampling for the determination of atmospheric mixing ratios of nonmethane hydrocarbons (NMHCs), selected halocarbons, and methyl nitrate was conducted aboard the National Center for Atmospheric Research (NCAR) C-130 aircraft over the Pacific and Southern Oceans as part of the First Aerosol Characterization Experiment (ACE 1) during November and December 1995. A latitudinal profile, flown from 76°N to 60°S, revealed latitudinal gradients for most trace gases. NMHC and halocarbon gases with predominantly anthropogenic sources, including ethane, ethyne, and tetrachloroethene, exhibited significantly higher mixing ratios in the northern hemisphere at all altitudes. Methyl chloride exhibited its lowest mixing ratios at the highest northern hemisphere latitudes, and the distributions of methyl nitrate and methyl iodide were consistent with tropical and subtropical oceanic sources. Layers containing continental air characteristic of aged biomass burning emissions were observed above about 3 km over the remote southern Pacific and near New Zealand between approximately 19°S and 43°S. These plumes originated from the west, possibly from fires in southern Africa. The month-long intensive investigation of the clean marine southern midlatitude troposphere south of Australia revealed decreases in the mixing ratios of ethane, ethyne, propane, and tetrachloroethene, consistent with their seasonal mixing ratio cycle. By contrast, increases in the average marine boundary layer concentrations of methyl iodide, methyl nitrate, and dimethyl sulfide (DMS) were observed as the season progressed to summer conditions. These increases were most appreciable in the region south of 44°S over Southern Ocean waters characterized as subantarctic and polar, indicating a seasonal increase in oceanic productivity for these gases.

1. Introduction

Halocarbon and nonmethane hydrocarbon (NMHC) gases are useful tracers of anthropogenic and biogenic emissions and for characterizing marine boundary layer (MBL) air [Davis *et al.*, 1996; Wingenter *et al.*, 1996]. NMHCs have also been employed as photochemical indicators of atmospheric hydroxyl (HO), atomic chlorine (Cl), and mixing [Roberts *et al.*, 1984; Blake *et al.*, 1993; Jobson *et al.*, 1994; McKeen *et*

al., 1996; Singh *et al.*, 1996; Wingenter *et al.*, 1996, this issue]. NMHCs and tetrachloroethene have diverse anthropogenic and natural emission sources and moderately short atmospheric lifetimes, resulting in significant latitudinal, seasonal, and vertical gradients [e.g., Blake and Rowland, 1986; Singh and Zimmerman, 1992; Rudolph, 1995; Wang *et al.*, 1995; Blake *et al.*, 1997]. The main sink of NMHC gases with an extractable hydrogen atom, such as ethane, as well as organic gases with an unsaturated bond, such as tetrachloroethene, is reaction with hydroxyl radicals (HO). Because HO is generated photochemically during daylight, its concentration varies diurnally and seasonally. Minimum HO levels are found in winter at high latitudes, resulting in significantly reduced removal rates for many trace gases. In the remote atmosphere, the most abundant NMHC compounds are the longest-lived group of light hydrocarbons (i.e., ethane, ethyne, and propane).

Significant concentrations of methyl nitrate (average atmospheric lifetime approximately 1 month) have also been detected in remote oceanic regions. Measurements at the Mauna Loa Observatory and during the Soviet-American Gas and Aerosol Experiment (SAGA 3) have suggested that the tropical ocean is a significant source of C₁-C₃ alkyl nitrates [Atlas *et al.*, 1992, 1993, 1997; Walega *et al.*, 1992; Ridley *et al.*, 1997]. However, the mechanism of production of methyl nitrate in seawater is not known [Atlas *et al.*, 1997]. Only the

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heavier alkyl nitrates ($>C_1$) are known to form photochemically in the atmosphere during the hydroxyl radical initiated oxidation of alkanes in the presence of NO_x [Darnall et al., 1976; Atkinson et al., 1982].

Methyl iodide is a metabolic product of many species of marine algae [Manley and de la Cuesta, 1997]; however, the details of exactly which species represent the most important producers are not well characterized. Previous studies have reported elevated atmospheric mixing ratios over coastal waters [e.g., Oram and Penkett, 1994], with macroalgae being a well-defined source [Manley and Dastoor, 1988; Nightingale et al., 1995; Laturus et al., 1998]. Manley and de la Cuesta [1997] have demonstrated that certain phytoplankton are sources; however, no sufficiently prolific organism has yet been found to explain measurements in pelagic surface waters [e.g., Singh et al., 1983; Nightingale, 1991; Moore and Tokarczyk, 1993]. Photochemical production of methyl iodide in seawater has been observed [Moore and Zafiriou, 1994] and may be a source of methyl iodide in the open ocean [Happell and Wallace, 1996]. Methyl iodide has a photolysis lifetime of about 3-4 days in the MBL at low latitudes, increasing to 2 weeks or more at higher latitudes.

Dimethylsulfide (DMS) is one component of an active seawater sulfur cycle and is secondarily produced by many phytoplankton species [Bates et al., 1994]. DMS can be lost from the water column by air-sea exchange, microbial consumption, or photochemical oxidation. The factors controlling the rate of DMS cycling in surface seawater, and hence its seawater concentration, strongly affect the amount of DMS that is released to the atmosphere. In addition to the concentration of DMS in seawater, atmospheric mixing ratios of DMS depend on chemical removal rates, boundary layer height, exchange with the free troposphere, and wind speed. The lifetime of DMS in the atmosphere is short, ranging from <1 day in the tropical MBL to several days at higher latitudes.

In this paper, we present atmospheric measurements of the concentrations of selected anthropogenic and biogenic halocarbons, light NMHCs, methyl nitrate, and DMS collected aboard the National Center for Atmospheric Research (NCAR) C-130 aircraft during the International Global Atmospheric Chemistry (IGAC) Project's First Aerosol Characterization Experiment (ACE 1). A complete rationale of the experiment and description of the research effort involving scientists

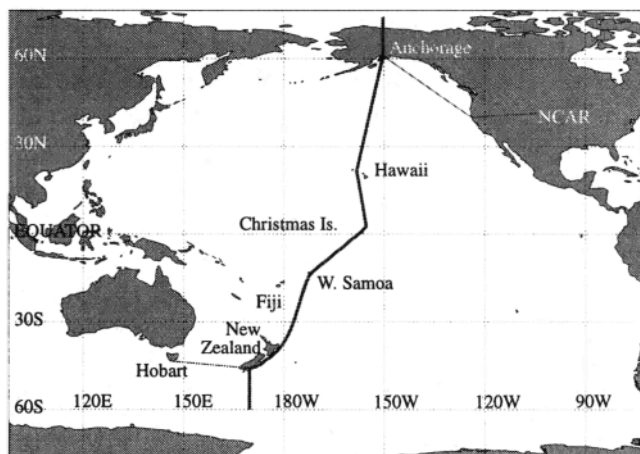


Figure 1a. NCAR C-130 flight tracks for the southbound latitudinal transit to Hobart, Australia, November 2-13, 1995.

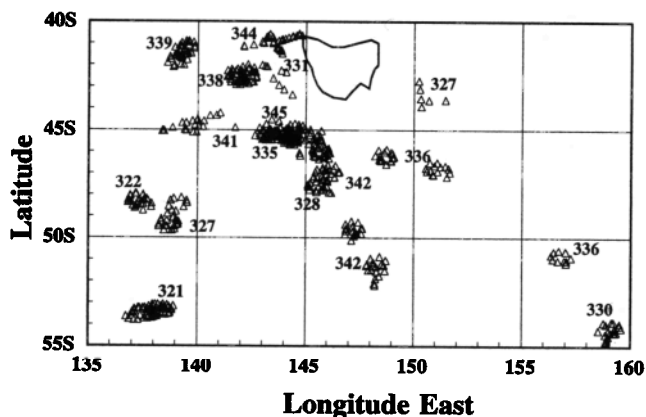


Figure 1b. Location of whole air samples collected aboard the C-130 at altitudes less than 0.5 km during the ACE 1 intensive period. The Julian Day at takeoff (UTC) is shown for each flight. December 1, 1995, was Julian Day 335.

from 45 research institutes in 11 countries is given by Bates et al. [1998a]. A southbound transit, made in early November between Alaska and Hobart, Tasmania, was designed for maximum latitudinal coverage (Figure 1a). The ACE 1 intensive experiment was conducted over the ocean south of Australia between November 18 and December 12, 1995 (Figure 1b). The experiment was timed to coincide with the seasonal maximum in DMS concentration, which occurs between November and March [Ayers et al., 1995; Bates et al., 1998a].

2. Experiment

A complete description of sampling procedures is given by Blake et al. [1992, 1994], and the experimental apparatus employed during ACE 1 is described by D. R. Blake et al. [1996], Sive [1998], and Sive et al. (manuscript in preparation, 1999). Both operations are summarized below. A metal bellows pump was used to fill evacuated sample canisters to a pressure of 40 psi, and the canisters were returned to the University of California, Irvine laboratory for analysis. Samples were usually analyzed within 1 week of collection and always in less than 2 weeks. A 1520 cm³ (STP) aliquot from each canister was preconcentrated cryogenically, split reproducibly into five portions, and the trace gas components in each aliquot were separated by gas chromatography. Selected C_1 - C_2 halocarbons were separated using a 60 m, 0.25 mm ID, DB-1 column with a 1 μ m film thickness (J & W Scientific) and detected with an electron capture detector (ECD). A portion of the effluent from this column was directed to a flame ionization detector (FID) for quantification of selected C_3 - C_{10} NMHCs. The light NMHCs (C_2 - C_5) were analyzed using a 50 m, 0.32 mm ID Al_2O_3/Na_2SO_4 porous layer open tubular (PLOT) column (Chrompack) coupled to an FID. A 60 m, 0.25 mm ID, 0.25 μ m film thickness Cyclodex-B column (J & W Scientific) and FID combination was used for selected C_6 - C_{10} NMHCs. An ECD detector and a 60 m, 0.25 mm ID, 0.5 μ m film thickness DB-5MS column (J & W Scientific) were used for the analysis of selected C_1 - C_2 halocarbons and methyl nitrate. A third ECD and a 60 m, 0.25 mm ID, DB-1/DB-5MS composite column (J & W Scientific), film thickness 0.25 μ m, were also employed

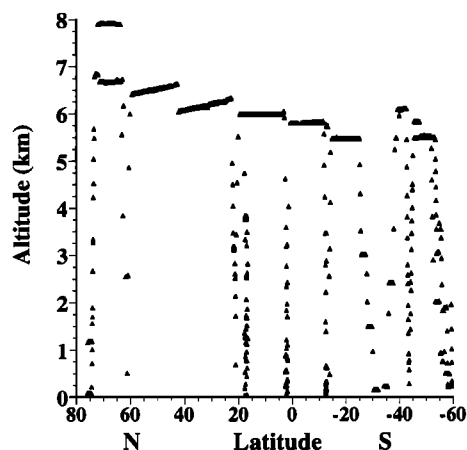


Figure 2. Location of whole air samples collected aboard the C-130 during the southbound latitudinal transit flights as a function of latitude and altitude.

for the determination of C_1 - C_2 halocarbons. The separation characteristics of each column were optimal for a particular subset of NMHC or halocarbon gases.

The limit of detection for the NMHCs was 3 parts per trillion by volume (pptv). Every sample contained methyl nitrate and each of the reported halocarbons at concentrations above their detection limits. The measurement precision was about 1% or 1.5 pptv (1σ) whichever is larger for the alkanes and alkynes, and 3% or 3 pptv (1σ) for the alkenes. For the halocarbons and methyl nitrate, the 1σ measurement precision in parentheses were as follows: methyl bromide (4%), methyl chloride (1.2%), methyl iodide (5%), tetrachloroethene (2%), and methyl nitrate (4%).

The accuracy and precision of the analytical system were closely monitored during the experimental period according to procedures described by Sive [1998] and B. C. Sive et al. (manuscript in preparation, 1999). We have participated in all five tasks of the National Science Foundation (NSF) sponsored Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE) overseen by Jack Calvert and Eric Apel at NCAR [Apel et al., 1994]. Results for the first five phases of NOMHICE demonstrate that our analytical procedures consistently yielded accurate identifications of the wide range of unknown hydrocarbons in the test samples and produced excellent quantitative results [Apel et al., 1994; Sive, 1998; B. C. Sive et al., manuscript in preparation, 1999].

DMS measurements were made in flight by isotopic dilution gas chromatography/mass spectrometry [Bandy et al., 1993]. The detection limit for DMS was 2 pptv.

The trajectories used in this study were calculated using the National Oceanic and Atmospheric Administration (NOAA)/Climate Monitoring and Diagnostics Laboratory's isentropic transport model [Harris and Kahl, 1994]. Input to the model consists of meteorological data from the European Centre for Medium-Range Weather Forecasts. Sources of uncertainty in isentropic trajectories include diabatic effects, observational errors, interpolation, assumptions about vertical motion, and sub-grid-scale phenomena. These have been discussed by Merrill [1996]. Because of these uncertainties, any individual trajectory may deviate from the actual path of an air parcel. Numerous studies, for example, Harris and Oltmans [1997], Harris et al. [1992], and Moody et

al. [1995], have used trajectories successfully to determine large-scale flow patterns affecting origins of air parcels.

3. Latitudinal Transect

The NCAR C-130 is based at the Research Aviation Facility in Broomfield, Colorado. In order to make maximum scientific use of the transit flights to Australia, the aircraft flew an extended latitudinal survey between 76°N and 60°S along the middle of the Pacific Basin following the route shown in Figure 1a. Figure 2 displays the latitude-altitude distribution of the 565 canister samples collected during these flights, which were made between November 2 and 13, 1995.

Three-dimensional color-coded concentration contour plots were generated from the ACE 1 hydrocarbon and halocarbon southbound latitudinal transit using the Stanford Graphics (SPC Software) statistical package. Regions where no samples were collected (see Figure 2) have been removed from the plot. The plots for ethane, ethyne, methyl chloride, tetrachloroethene, methyl iodide, and methyl nitrate are shown in Plates 1-6, respectively. The wide range of mixing ratios observed for these gases during the transit flights prescribed the use of logarithmic mixing ratio scales.

The trace gas distributions displayed in Plates 1-6 provide a useful perspective for characterizing large-scale regional features encountered during the ACE 1 transect. However, the atmospheric sampling was neither uniform nor completely random. Therefore, when these plates are being interpreted, reference should be made to the canister sampling distribution illustrated in Figure 2. Data collected downwind of Hawaii on flights 4 and 5 during studies of the Kilauea volcanic plume were not included as they contained significant enhancements in fresh pollutants from local Hawaiian urban areas. During one of the two approaches into Christchurch, New Zealand, we again sampled freshly emitted urban pollutants, leading to the removal of three additional samples from the database employed for Plates 1-6 (but which remain in the archive version of the data set).

3.1. Latitudinal Gradients

The color contour plots in Plates 1, 2, and 4 illustrate the strong latitudinal gradient in mixing ratios of the gases ethane, ethyne, and tetrachloroethene, with their highest concentrations at high latitudes in the northern hemisphere and relatively low concentrations in equatorial regions and the southern hemisphere. This is consistent with our knowledge of the urban/industrial sources of these gases and with previous measurements made at the surface [Blake and Rowland, 1986; Singh and Zimmerman, 1992; Rudolph, 1995; Wang et al., 1995] and from aircraft [D. R. Blake et al., 1996; Blake et al., 1997]. By contrast, Plate 3 shows that at low altitude between 75°N and 50°N, methyl chloride exhibits the lowest mixing ratios observed aboard the C-130 during the entire experiment. This trend is similar to previous observations of low methyl chloride mixing ratios at low altitudes over the western Pacific basin during September and October 1991 [Blake et al., 1997] and is possibly linked to ocean undersaturation at high latitudes as reported by Moore et al. [1996].

At the highest latitudes (75°N-60°N) and the aircraft cruising altitude, mixing ratios of the long-lived NMHCs ethane and ethyne were about 1000 and 200 pptv, respectively

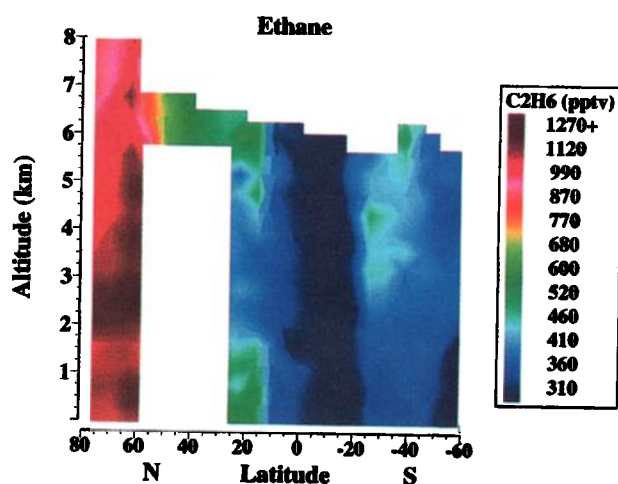


Plate 1. Color contour plot showing the mixing ratio of ethane during the southbound latitudinal transit flights as a function of latitude and altitude.

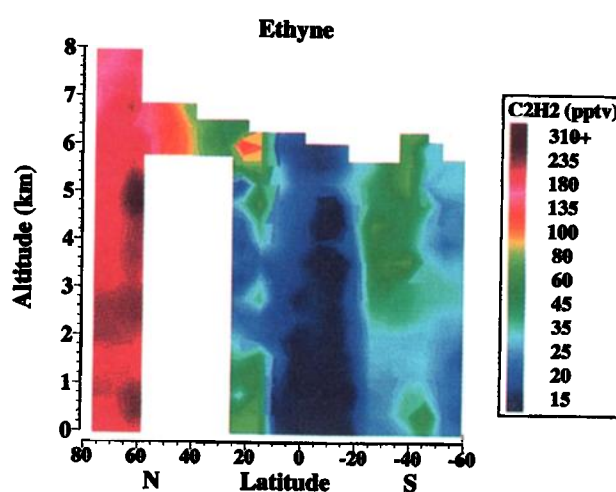


Plate 2. Same as for Plate 1, but for ethyne.

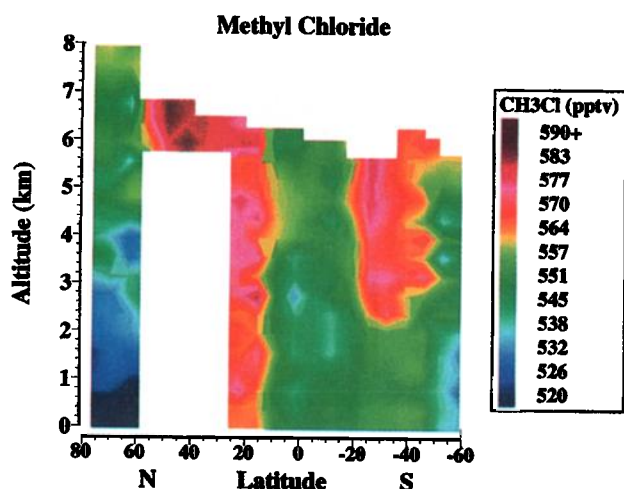


Plate 3. Same as for Plate 1, but for methyl chloride.

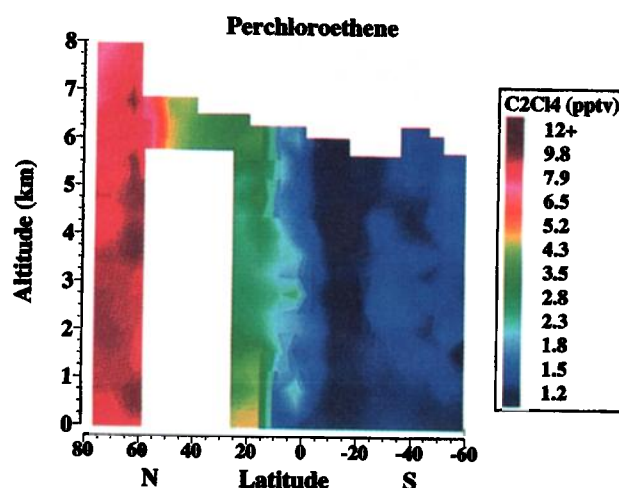


Plate 4. Same as for Plate 1, but for tetrachloroethene.

(Plates 1 and 2). Relatively short-lived gases, including ethene and toluene (both having average lifetimes in that region and season of about 1 week) were observed at low mixing ratios of about 30 and 10 pptv, respectively. Average toluene/benzene ratios were also low (≈ 0.2) compared to a typical urban source ratio of approximately 2.7 [Seila *et al.*, 1989]. Low ratios are caused by faster photochemical removal of toluene relative to benzene (approximately 5 times faster), as well as by mixing with background air [McKeen *et al.*, 1996] during long-range transport, and indicate that the air was significantly aged. Ozone mixing ratios as high as 70 ppbv imply that the observed pollution was associated with in situ ozone production. Our 10-day back trajectory calculations suggest that the air mass originated at very high northern latitudes, including northern parts of Asia and possibly northern Europe, but had spent many days over the North Pacific and Arctic Oceans before sampling.

At 6–7 km altitude between 60°N and 20°N, a gradual decrease in the mixing ratios of ethane, ethyne (Plates 1 and 2), and the industrial tracers tetrachloroethene (Plate 4) and methyl chloroform (not shown) was observed. The mixing ratios of benzene, ethene, and toluene decreased to 10 pptv or less as a result of the advanced photochemical age of the air

mass. By contrast, relatively high levels of the biomass burning tracer methyl chloride (Plate 3) were observed. The increased methyl chloride, and decreasing tetrachloroethene and methyl chloroform, was associated with a shift to a more southerly continental Asian origin for the sampled air mass. This trace gas signature is consistent with a regional source similar to that observed previously for southern Asia [Blake *et al.*, 1997].

South of about 10°N, the mixing ratios of the gases in Plates 1–4 decrease even further at all altitudes to very low levels just south of the equator. Average mixing ratios between 0° and 13°S were approximately 305 pptv for ethane, 16 pptv for ethyne, 555 pptv for methyl chloride (Figure 3), and 5 pptv for benzene. The shorter-lived gases, including ethene and toluene, were below the detection limit. These low values correspond with a transition to slow moving equatorial clean marine air, frequently originating in the southern hemisphere.

3.2. Biomass Burning

Plates 1–3 and Figure 3 show that during the flight from Western Samoa to Christchurch, New Zealand, the air sampled at low altitude exhibited clean southern hemispheric mixing

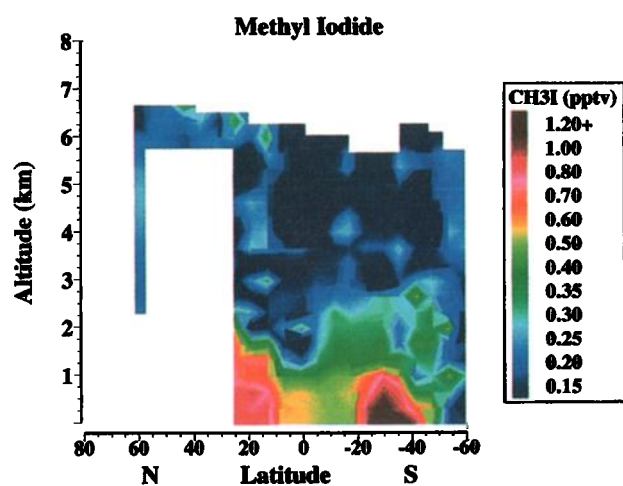


Plate 5. Same as for Plate 1, but for methyl iodide

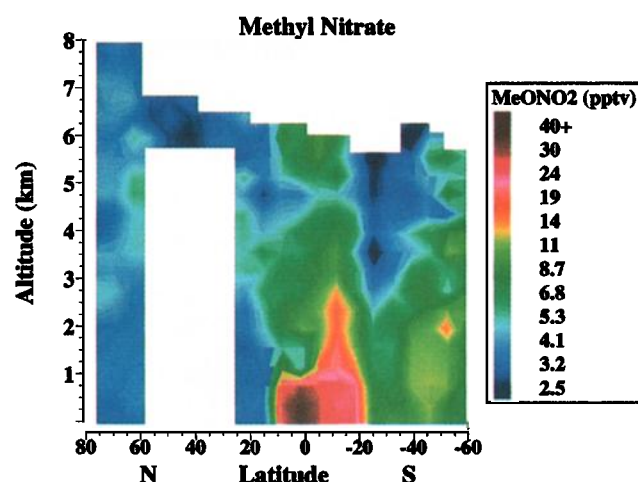


Plate 6. Same as for Plate 1, but for methyl nitrate.

ratios (mean ethane 360 pptv, ethyne 30 pptv, and methyl chloride 555 pptv). However, at the aircraft cruising altitude of 5.5 km the C-130 encountered polluted continental air at approximately 19°S, with variable mixing ratios of several trace gases that were significantly elevated above background levels. Peak mixing ratios were 630 pptv for ethane, 70 pptv for ethyne, and 595 pptv for methyl chloride (Figure 3 and Plates 1-3). *Kok et al.* [1998] also report enhanced CO in this region and ozone levels as high as 95 ppbv. However, the mixing ratios of propane, tetrachloroethene (Figure 3), and methyl chloroform (not shown) were not elevated above their background mixing ratios. The individual plumes were observed to extend for about 450 km and 280 km in a north-south direction until the aircraft descended below 3 km at 28°S (Figure 3).

Continental air was again sampled farther south when the aircraft ascended through 4 km at 38°S, near the northern tip of New Zealand. Ethane, ethyne, and methyl chloride mixing ratios were above background levels (Figure 3). Peak ozone was about 80 ppbv. Propane exhibited a slight increase to approximately 25 pptv. These enhancements were sampled for a distance of about 600 km until the C-130 descended through 3 km at 43°S. This more southerly plume air was

characterized by relatively lower methyl chloride enhancements (Figure 3), but the absence of urban/industrial halocarbon tracers indicates that each of these polluted air masses originated as emissions from continental biomass burning, rather than urban combustion.

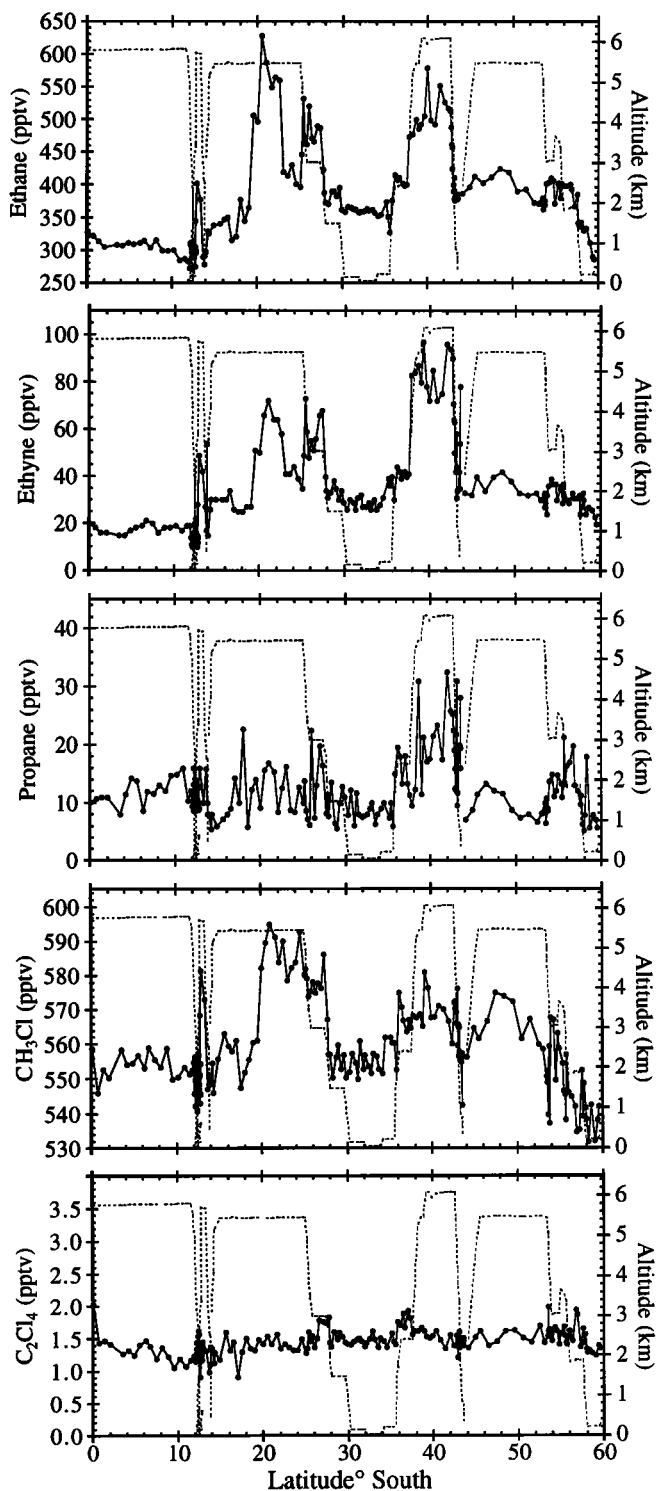


Figure 3. Ethane, ethyne, propane, methyl chloride, and tetrachloroethene (solid line), and altitude (dashed line) versus latitude in the southern hemisphere during the November 9-13 transit flights. These flights landed in Western Samoa (14°S) and Christchurch, New Zealand (44°S).

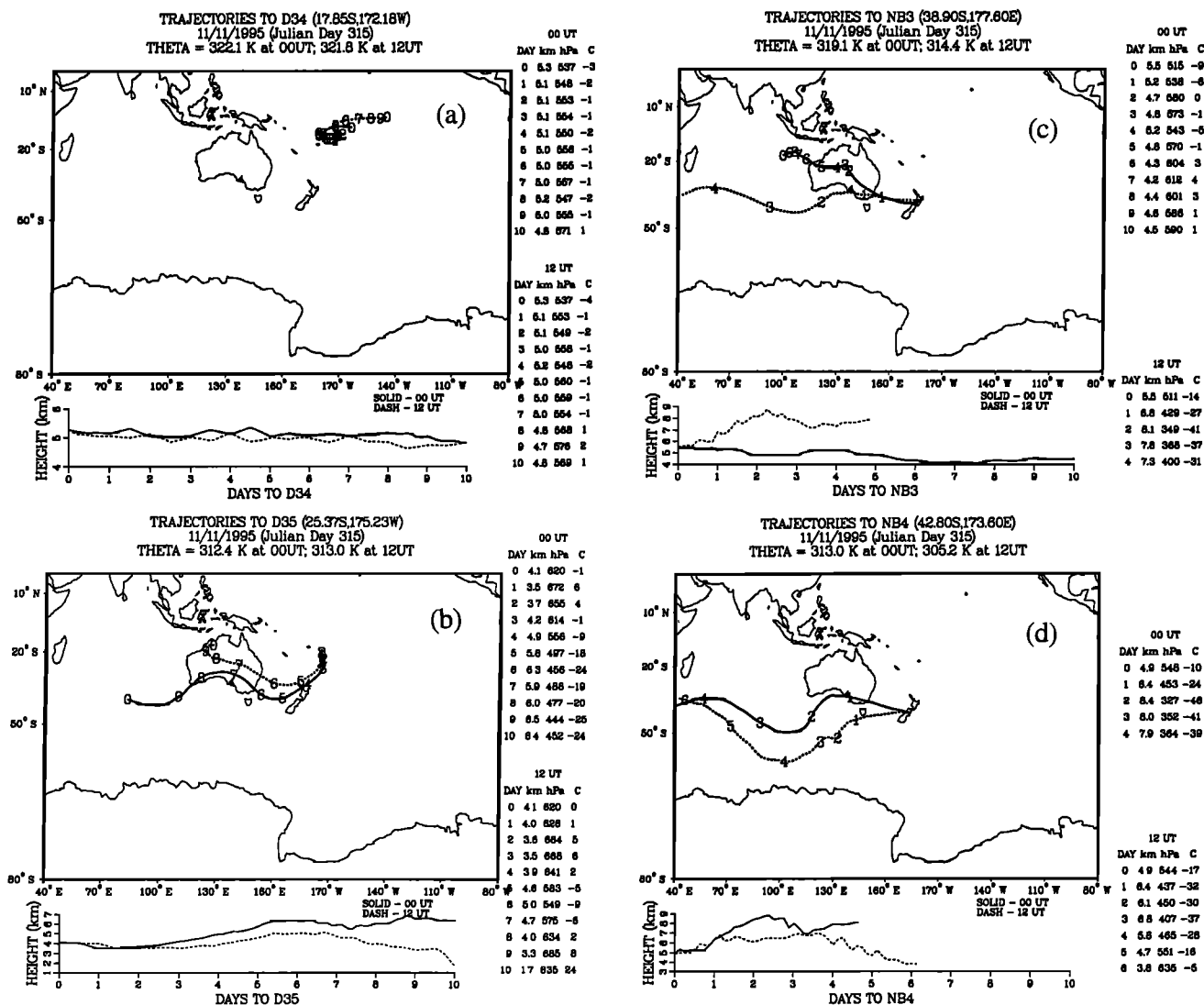


Figure 4. Selected 10-day back trajectories in (a) the high-altitude clean background region and (b-d) three different locations within the polluted region during flight 8, November 10-11, 1995. The sampling times for the trajectory locations were (a) 2150 UT on November 10, 1995; (b) 2335 UT on November 10, 1995; (c) 0320 UT on November 11, 1995; and (d) 0437 UT on November 11, 1995. The solid 0000 UT trajectories are therefore closest to the actual sampling times.

Although propane, benzene, n-butane, and toluene are emitted in significant quantities (along with ethane and ethyne) during biomass burning [e.g., *N. J. Blake et al.*, 1996], their mixing ratios were near or at background levels in the plume layers. This indicates that the transport times for the sampled air masses were long compared to their local atmospheric lifetimes (approximately 13 days in the midtroposphere for propane, 9 days for benzene, 6 days for n-butane, and 1 day for toluene), and is consistent with travel times of the order of 3 weeks.

Ratios of ethyne/ethane were about 0.10–0.15 pptv/pptv in the 19°–28°S plumes and slightly higher (0.15–0.20 pptv/pptv) in the 38°–43°S plume, but all were significantly lower than average ratios of approximately 0.5 pptv/pptv found in active fire regions [*N. J. Blake et al.*, 1996]. The photochemical lifetime of ethane is almost 4 times longer than that of ethyne, so these low ethyne/ethane ratios are consistent with the air masses being considerably aged during

long transport times from the source regions. The observed ethyne/CO ratios in the range 0.5–1.0 pptv/ppbv were also low, with the slightly fresher southern plume toward the higher end of the range. Ethyne/CO ratios of 1.0 pptv/ppbv or less imply that these biomass burning emissions have been aged >5 days [e.g., *Sandholm et al.*, 1992; *Smyth et al.*, 1996; *Gregory et al.*, 1999]. In addition, the elevated ozone levels, which were more than 200% above background levels, are consistent with photochemical aging accompanied by in situ ozone production.

The emission ratio of methyl chloride from individual fires is controlled by the amount of chloride present in the fuel [*Reinhardt*, 1987]. This might help explain the lower methyl chloride in the more southerly plume (Figure 3), even though this air mass appears to have been somewhat less aged by transport and dilution during transport.

Several 10-day back trajectories have been calculated for different points during the flight track and are shown in

Figures 4a-d. Figure 4a exhibits an easterly back trajectory into the central Pacific, consistent with the clean marine nature of the sampled air. The other three trajectories (Figures 4b-d) represent polluted continental air. Figures 4b and 4d show trajectories that follow the air back over Australia to midway into the Indian Ocean after 10 days. Figure 4d displays a much faster moving descending air mass originating even farther west. This trajectory also only just touches the southern tip of Australia. Given the very aged chemical characteristics of the plumes and the westerly trajectory paths, it may be possible that the products from biomass burning were introduced as far away as the South Atlantic region (southern Africa and South America). However, Australian biomass burning can not be ruled out as a source for at least some of the enhancements.

Although data for 1995 are not presently available, NOAA 11 satellite advanced very high resolution radiometer (AVHRR) images for November 1992 and 1993 reveal that a significant number of fires occur in Australia during this time of year. However, these were principally confined to the northern regions of the country. Southern African biomass burning activity typically peaks between July and September [Justice *et al.*, 1996], but AVHRR images show that a significant number of fires continued into November 1992 and 1993. Measurements made as part of the TRACE A/SAFARI experiment [Fishman *et al.*, 1996] demonstrated that widespread biomass burning in both South America and southern Africa was the dominant source of ozone precursors to the South Atlantic region during September-October 1992.

Matsueda *et al.* [1998] report measurements of CO in the upper troposphere over the western Pacific which reveal a strong seasonal maximum in CO mixing ratios in the latitude range 20-30°S during October and November of 1994 and 1995. Air mass back trajectories indicate that CO-rich air from biomass burning in South America or southern Africa was injected into the free troposphere by convection and rapidly transported over the Indian Ocean into the western Pacific. Matsueda *et al.* [1998] conclude that this transport is much more frequent during the October-November transitional period from the dry season to the wet season because of the onset of more active deep convection in the continental source regions.

Continental plumes with trace gas characteristics similar to those encountered during the ACE 1 transit flights were frequently observed over the southwestern Pacific during NASA's Pacific Exploratory Mission-Tropics A (PEM-Tropics A) aircraft campaign during September-October 1996 [Hoell *et al.*, 1999; Schultz *et al.*, 1999; Talbot *et al.*, 1999; Blake *et al.*, 1999]. These polluted air masses originated from biomass burning emissions in southern Africa and South America [Fuelberg *et al.*, 1999] and were so prevalent that they had a considerable impact on the ozone budget of the tropical troposphere [Schultz *et al.*, 1999]. The PEM-Tropics A observations combined with those of Matsueda *et al.* [1998] indicate that the high levels of trace gases, including ozone measured during ACE 1, represent a seasonal perturbation of the southwestern Pacific region. The PEM-Tropics A and ACE 1 results are compared in detail by Blake *et al.* [1999].

3.3. Methyl Iodide and Methyl Nitrate

The latitudinal distributions of methyl iodide and methyl nitrate shown in Plates 5 and 6 are notably different from the

distributions of ethane, ethyne, methyl chloride, and tetrachloroethene displayed in Plates 1-4. The strong negative vertical gradients exhibited by both methyl iodide and methyl nitrate reflect the dominance of their oceanic sources [Loveloock *et al.*, 1973; Singh *et al.*, 1983; Chameides and Davis, 1980; Atlas *et al.*, 1992, 1993, 1997; Walega *et al.*, 1992]. However, the latitudinal variations of the two gases reveal very different characteristics. Two methyl iodide "hot spots" are displayed in Plate 5, one each side of the equator in tropical/subtropical regions. The first hot spot represents samples collected at low altitude near Hawaii (approximately 15°-20°N). The other was encountered in the MBL between 30°S and 35°S during the flight from Western Samoa to Christchurch, New Zealand. At nearly 2 pptv, the methyl iodide mixing ratios in this region were the highest measured from the C-130 during the entire ACE 1 experiment. By contrast, very low levels of methyl iodide were measured in the MBL between 55°S and 60°S during the flight south from Christchurch, indicating that in mid-November these Antarctic waters emit very little methyl iodide.

In the case of methyl nitrate, maximum concentrations were found over the equatorial regions of the Pacific. Mixing ratios as high as 50 pptv were measured in the MBL near Christmas Island (1°-3°N). Enhanced concentrations (20-35 pptv) were also observed near Western Samoa (at approximately 13°S).

The equatorial portions of these latitudinal profiles are similar to those from the SAGA 3 equatorial Pacific cruise. Although methyl nitrate was not measured during SAGA 3, Atlas *et al.* [1993] did find a broad maximum in the atmospheric mixing ratios of the C₂ and C₃ alkyl nitrates centering near the equator. These maxima were well-correlated with maxima in chlorophyll and nitrate, which are oceanographic indicators of enhanced upwelling and marine productivity. They concluded that there was a possible oceanic source for these alkyl nitrates related to biogenic production. In addition, these measurements were not correlated with their corresponding latitudinal observations for methyl iodide, which instead showed elevated atmospheric concentrations near 5°-10°N. Thus the ACE 1 results support the suggestion by Atlas *et al.* [1993] that marine methyl iodide production is not necessarily coupled to the formation and emission of other biogenically produced trace gases.

Plates 5 and 6 also reveal slight enhancements in methyl nitrate, but not in methyl iodide, in the free troposphere near the equator up to the maximum aircraft cruise altitude. The fact that methyl nitrate, but not methyl iodide, is enhanced may be associated with the actively convective equatorial location of the low-altitude methyl nitrate enhancements. Methyl nitrate also has a substantially longer atmospheric lifetime of about 1 month compared with about 3 days for methyl iodide at the equator. Thus methyl nitrate would be expected to persist in the free troposphere much longer than methyl iodide after any convective event.

The fact that methyl iodide and methyl nitrate both clearly originate from the ocean, while exhibiting markedly different distributions, serves to illustrate the complexity of oceanic production mechanisms and air-sea exchange processes.

Plate 6 reveals very low mixing ratio values for methyl nitrate (lifetime similar to ethyne) in the region of the continental plumes. This illustrates the lack of continental sources for this gas and indicates that biomass burning is not a major source of methyl nitrate, in agreement with Lobert *et al.* [1990] and Flocke *et al.* [1991].

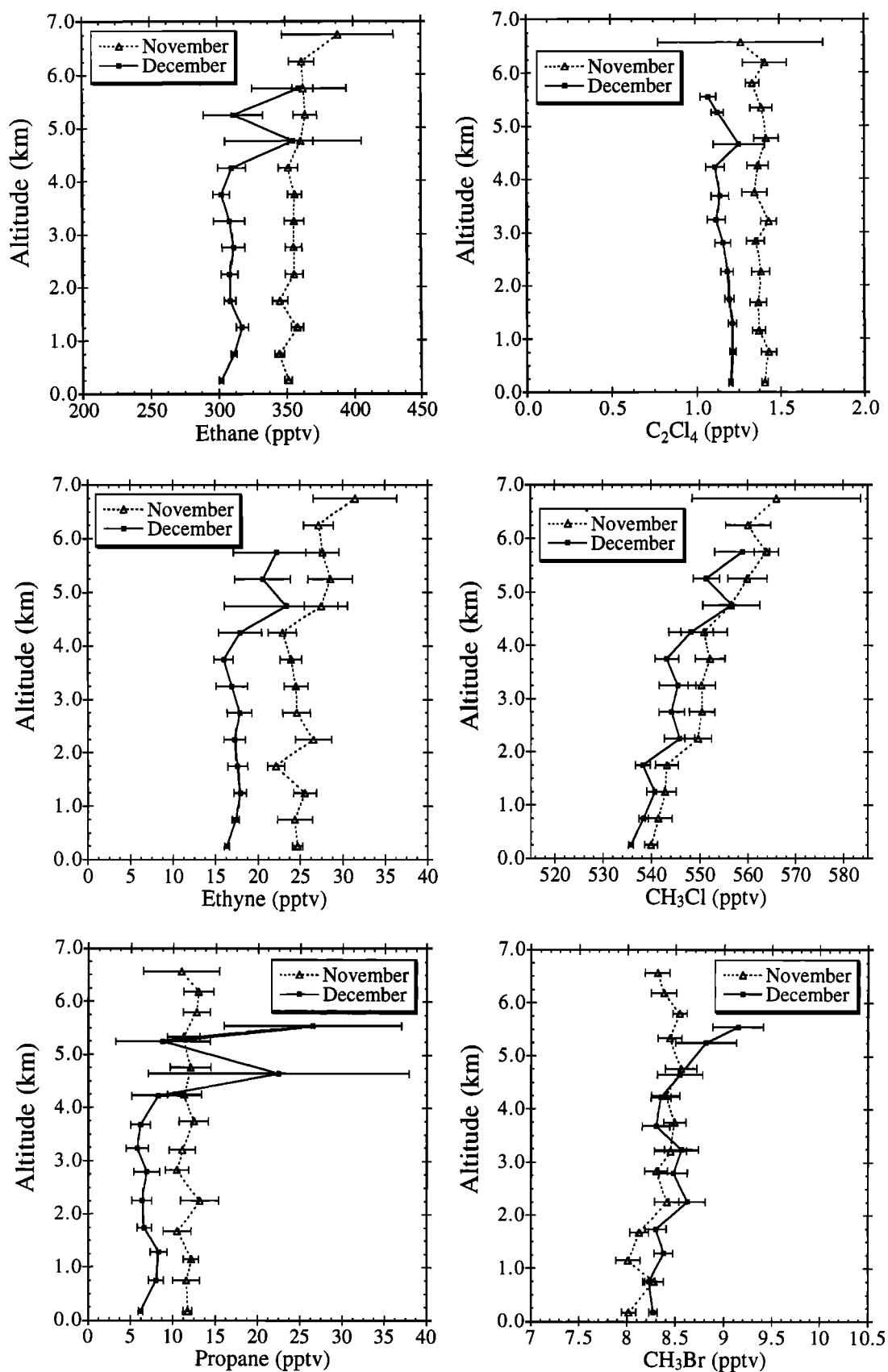


Figure 5. Mean vertical profiles of selected trace gases for November and December at high southern latitudes ($>40^{\circ}S$) during the ACE 1 intensive experiment. Error bars represent the 95% confidence level of the mean.

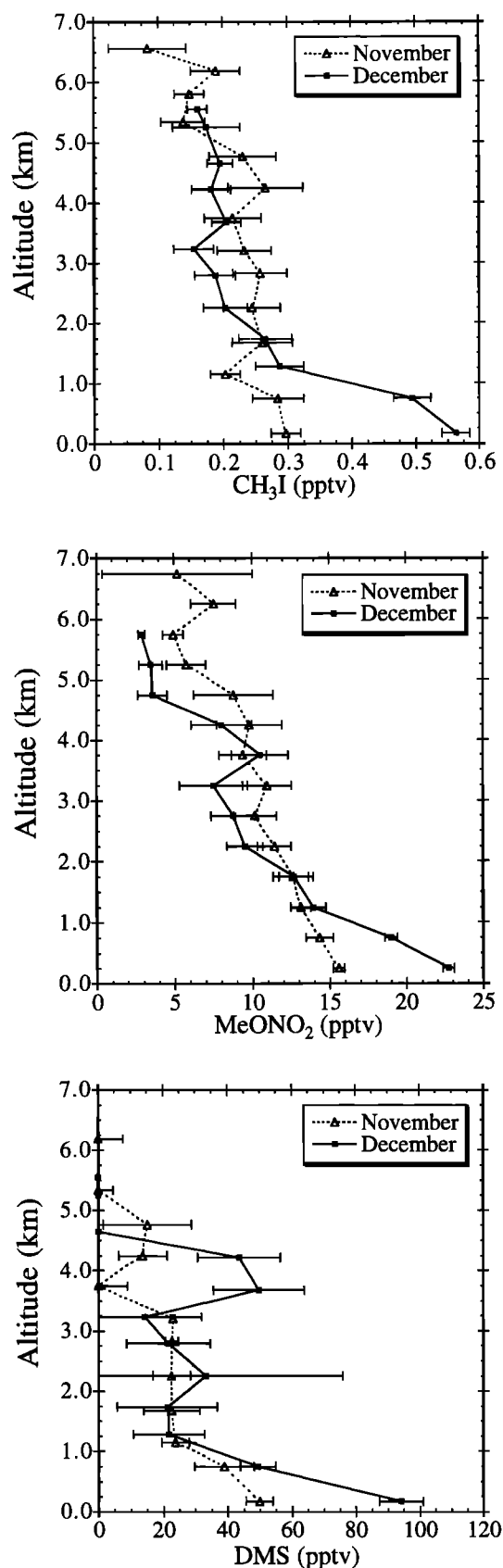


Figure 6. Mean vertical profiles of methyl iodide, methyl nitrate, and DMS for November and December at high southern latitudes ($>40^{\circ}\text{S}$) during the ACE 1 intensive experiment. Error bars represent the 95% confidence level of the mean.

4. Hobart Intensive

The C-130 aircraft operated out of Hobart, Tasmania, in the region between 40°S and 55°S from November 18 to December 12. More than 1400 canister samples were collected during this period. The location of samples collected at altitudes less than 0.5 km are shown in Figure 1b. Westerly marine airflow dominates the study region. A long wave trough was present for much of the Hobart intensive portion of the ACE 1 experiment, causing cold front activity to be generally above average, with below average temperatures, pressures, and rainfall [Hainsworth *et al.*, 1998].

4.1. Vertical Distribution of Anthropogenic Gases

The trace gas mixing ratios for all samples collected in the ACE 1 intensive study region ($>40^{\circ}\text{S}$) during the late November and early December periods were binned by 0.5 km altitude increments. The averages for these bins for selected trace gases are plotted in Figure 5. Average mixing ratios for all the gases shown in Figure 5 are characteristic of clean marine conditions in the southern hemisphere.

The only NMHC gases that were usually observed at mixing ratios above the limit of detection of our instrumental method were ethane, ethyne, and propane. Benzene mixing ratios were lower than the detection limit in nearly 20% of samples, particularly during the later part of the intensive period. Greater than 80% of samples contained ethene levels below the detection limit, and ethene was less than 10 pptv in all but seven samples. Levels of the gases propene, i-butane, n-butane, i-pentane, n-pentane, and toluene were below their detection limits in more than 95% of the samples. The remaining $\text{C}_3\text{-C}_{10}$ saturated and unsaturated hydrocarbons were always less the 3 pptv detection limit. Model calculations using these low NMHC levels are in excellent agreement with measured OH concentrations [Suhre *et al.*, 1998; Sive, 1998; Wingenter, 1998; Wingenter *et al.*, this issue].

For gases with principally anthropogenic sources, such as ethane, ethyne, propane, and C_2Cl_4 , the low variability in their mixing ratios at the 95% confidence level of the mean (Figure 5) indicates that local and regional pollution sources made very little impact at altitudes less than 4 km. Fewer samples were collected at altitudes above 4 km, resulting in larger error bars for many gases. Some of these high-altitude samples contained relatively high levels of propane and ethane, possibly from long-range transport from sources such as natural gas and liquefied petroleum gas, contributing to the variability shown in Figure 5 [D. R. Blake *et al.*, 1996; Blake and Rowland, 1995]. Although distant biomass burning emissions may have had an impact on the relatively long-lived gases methyl chloride and methyl bromide at lower altitudes (see below), transit times were too long to have influenced the NMHCs. In general, the air masses encountered south of Hobart during the ACE 1 intensive period were highly aged. For example, ethyne/CO ratios were less than 0.7 pptv/ppbv for all free tropospheric samples, and 80% were less than 0.4 pptv/ppbv. Typical MBL ethyne/CO ratios were 0.2–0.4 pptv/ppbv.

The average vertical profiles shown in Figure 5 reveal that there was a uniform decrease in the mixing ratios of ethane, ethyne, propane, and tetrachloroethene between late November and early December, at least up to an altitude of 4

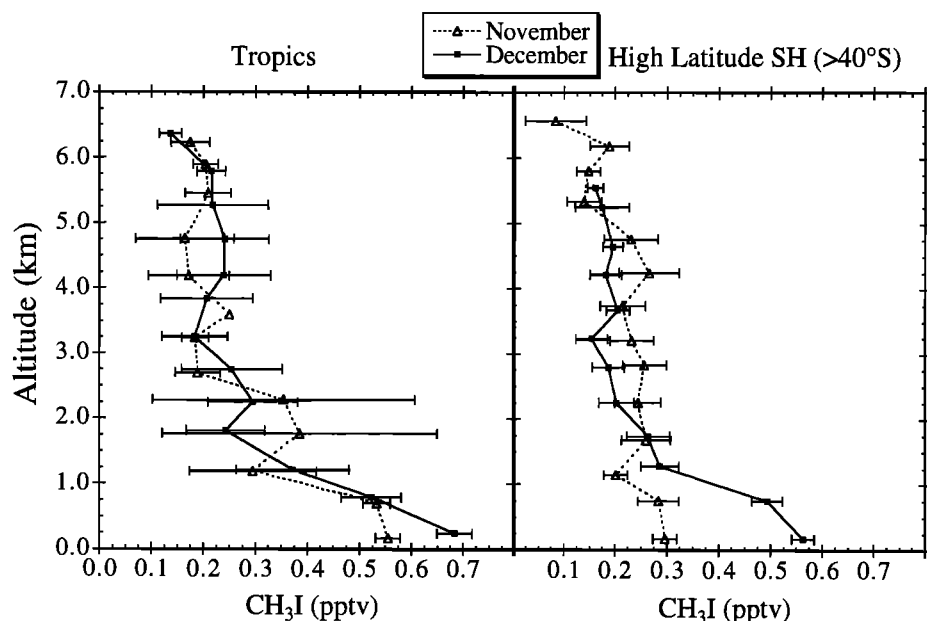


Figure 7. Mean vertical profiles of methyl iodide for November and December over the remote tropical Pacific and at high southern latitudes (>40°S) during the ACE 1 intensive experiment. Error bars represent the 95% confidence level of the mean.

km. These decreases are consistent with the expected mixing ratio decline associated with seasonally increasing hydroxyl mixing ratios. The measured mixing ratios and trends for ethane and ethyne are similar to previous surface observations made on the Antarctic continent by *Rudolph et al.* [1989]. However, the mixing ratios reported by *Rudolph et al.* [1989] for propane were significantly higher (about 70 pptv compared with 5–15 pptv for this work). Average concentrations of HO and Cl required to reproduce the observed seasonal decreases in the mixing ratios of ethane, ethyne, propane, and tetrachloroethene have been calculated by *Wingenter et al.* [this issue]. *Sive* [1998] presents photochemical removal of ethane on a shorter, Lagrangian experiment timescale.

The mixing ratio of methyl chloride decreased by nearly 5 pptv between late November and early December (Figure 5). This is only about half of the expected decline if we were to assume that the region was completely isolated from methyl chloride sources. Figure 5 also illustrates a significant positive vertical gradient for methyl chloride, which persisted for the entire Hobart intensive period. This gradient is most likely caused by the long range transport of air containing enhanced levels of long-lived methyl chloride, possibly from distant biomass burning sources, in combination with a relative lack of sources in the study region.

Methyl bromide also has a positive vertical gradient (Figure 5), with an average free tropospheric mixing ratio 0.3 pptv higher than in the MBL. Seasonal input from distant biomass burning sources is the most likely cause of this gradient, and appears to obscure the expected seasonal decrease in methyl bromide [*Wingenter*, 1998; *O. W. Wingenter et al.*, manuscript in preparation, 1999]. *Wingenter* [1998] and *O. W. Wingenter et al.* (manuscript in preparation, 1999) have further calculated that the Southern Ocean does not appear to be a net source or sink of methyl bromide during the studied period.

4.2. Vertical and Spatial Distribution of Oceanic Gases

The average vertical profiles for methyl iodide, methyl nitrate, and the corresponding in situ DMS measurements are shown in Figure 6. In November, DMS mixing ratios were enhanced in the MBL, methyl nitrate is only slightly enhanced, and methyl iodide shows no significant MBL enhancements. However, in December, all three gases reveal enhancements in their MBL mixing ratios, reflecting their oceanic sources. For the samples collected at altitudes less than 0.5 km, the mixing ratios of both methyl iodide and DMS nearly doubled during this short period. The average methyl iodide mixing ratio in the MBL in late November was 0.30 pptv, compared with a value of 0.56 pptv in early December. Average mixing ratios of methyl nitrate increased by about 50% from approximately 15 pptv to nearly 23 pptv. The corresponding DMS averages were 50 pptv and 95 pptv.

The seasonal mixing ratio increase for methyl iodide, methyl nitrate, and DMS within the MBL corresponds to the onset of summer in the southern hemisphere. Increased sunlight and surface water temperatures are two of the many factors that may influence marine production/emission of these gases.

Figure 7 compares tropical and high-latitude southern hemisphere mixing ratios of methyl iodide. Substantially fewer samples were collected in the tropics, resulting in generally larger uncertainties in the mean. However, Figure 7 shows that the average mixing ratios for methyl iodide within the MBL in December were very similar to those found in the tropical MBL. This comparison also shows very little change in average methyl iodide mixing ratios in the tropics for the two latitudinal transits. The northbound December transit went via Fiji instead of Samoa, but both transits were routed through Christmas Island and Hawaii (Figure 1a).

The spatial distributions of methyl iodide, methyl nitrate,

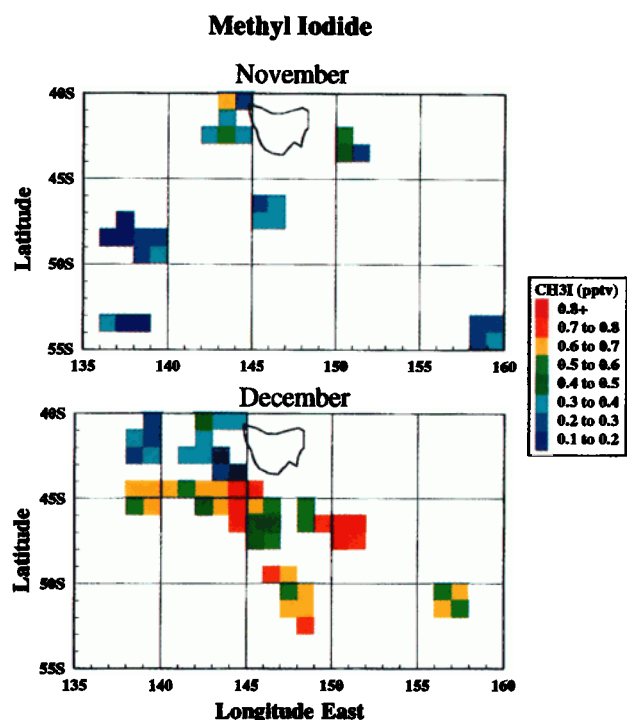


Plate 7. Mixing ratio distribution of methyl iodide for altitudes less than 0.5 km during November and December as a function of latitude and longitude.

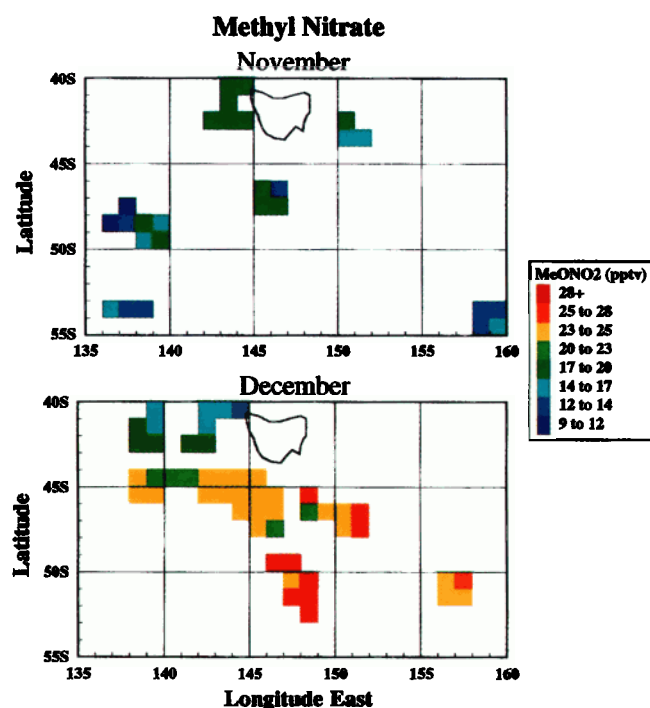


Plate 8. Same as for Plate 7, but for methyl nitrate.

and DMS in the MBL for the late November and early December ACE 1 intensive periods are plotted in Plates 7-9. To construct these plots, 1° latitude by 1° longitude mixing ratio averages were calculated including all samples collected at altitudes less than 0.5 km during the flights as shown in Figure 1b.

Plates 7-9 reveal no strong spatial trend in MBL mixing ratios of methyl iodide, methyl nitrate, and DMS during November except for somewhat higher levels of DMS to the north, particularly near Cape Grim. By contrast, during December generally greater, and more variable, mixing ratios were observed for methyl iodide, methyl nitrate, and DMS. A pronounced latitudinal trend, with an abrupt increase in mixing ratio south of about 44°S, was observed for all three gases. No latitudinal gradient was observed for any of the other halocarbon or NMHC gases that we measured.

To investigate the latitudinal trend observed for methyl iodide, methyl nitrate, and DMS, all data collected in December were separated by latitude into subsets of <44°S (40°-44°S) and >44°S (44°-55°S) and plotted versus altitude in Figure 8. Figure 8 shows that at altitudes less than about 0.5 km the mixing ratios of methyl iodide, methyl nitrate, and DMS were consistently lower in the <44°S region compared with the region to the south. Figure 8 also illustrates that much of the variability in the December mixing ratio seen in both Figure 6 and Plates 7-9 can be accounted for by the latitudinal transition at 44°S.

In the <44°S region, relatively high mixing ratios of methyl nitrate and DMS were observed between 2 and 4 km compared with this same altitudes at higher latitudes (Figure 8). The enhanced samples were collected during a single flight (flight 27), which focused on sampling the outflow from large developed cumulus clouds [Clarke *et al.*, 1998]. Free tropospheric mixing ratios of methyl nitrate and DMS during this flight were similar to MBL levels, illustrating the effect of fast vertical transport of reactive marine gases, including DMS, from the MBL into the free troposphere. By contrast, the flights made at latitudes >44°S during December took place under clear skies and included the Lagrangian B series of flights which were made in a clear-air region of postfrontal subsidence [Wang *et al.*, this issue]. These stable conditions resulted in the relatively low free tropospheric mixing ratios

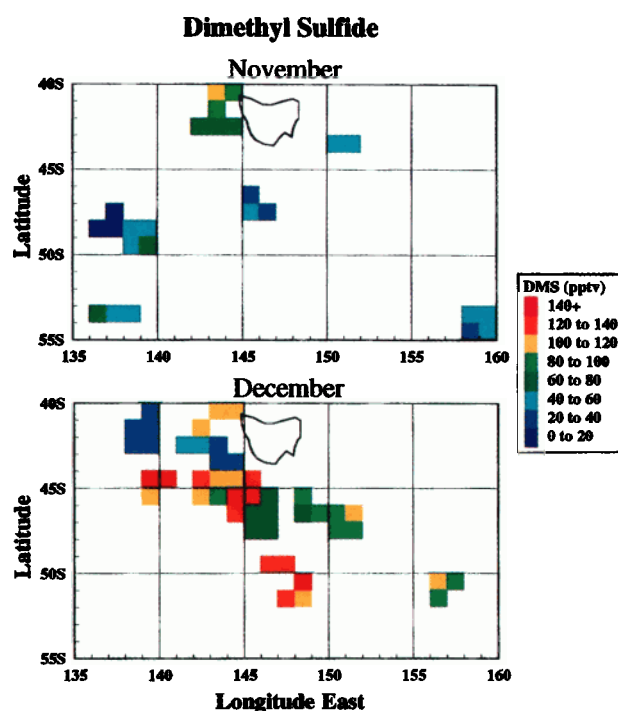


Plate 9. Same as for Plate 7, but for DMS.

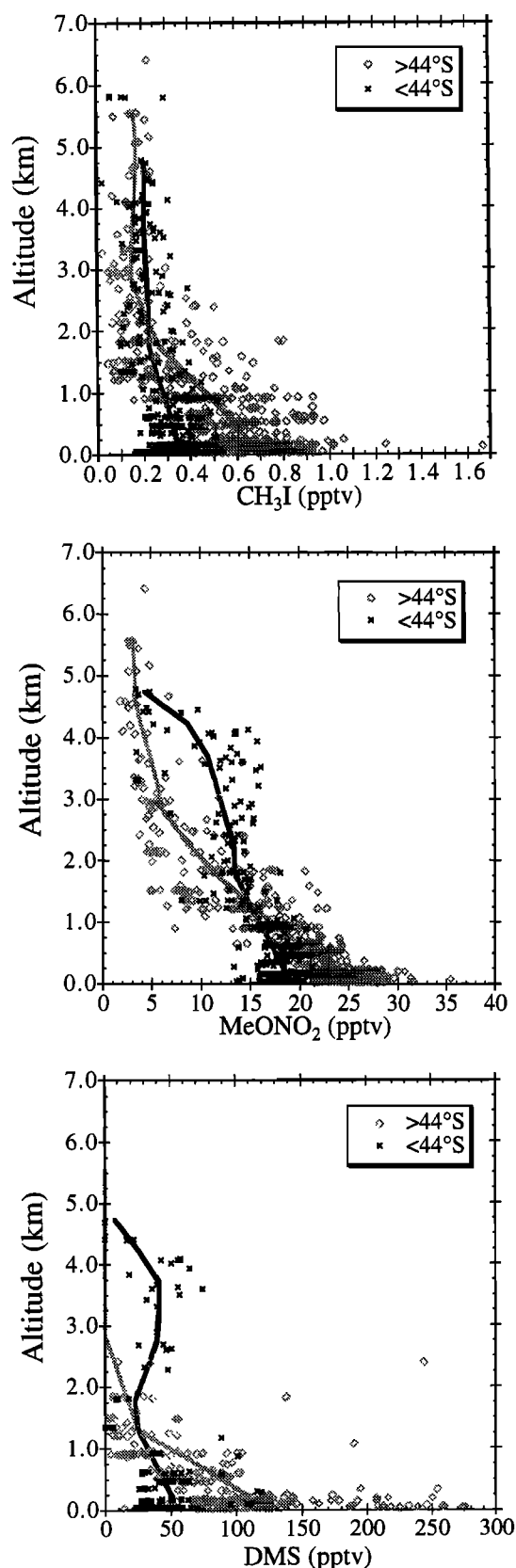


Figure 8. Vertical distribution and smoothed average profiles of methyl iodide, methyl nitrate, and DMS for December at latitudes $>44^{\circ}\text{S}$ (40° – 44°S) and $<44^{\circ}\text{S}$ (44° – 55°S) during the ACE 1 intensive experiment.

observed for methyl iodide, methyl nitrate, and DMS at latitudes $>44^{\circ}\text{S}$ (Figure 8).

The atmospheric mixing ratio transition at 44°S closely corresponds to a major water mass boundary change from oceanic subtropical convergence zone water to colder subantarctic water [Bates *et al.*, 1998a, b]. Bates *et al.* [1998b] defines the surface water masses by salinity, with subtropical convergence zone salinities >34.8 and subantarctic water salinities in the range 34.2–34.8. Even colder and fresher polar waters were located south of about 50°S (salinity <34.2). Oceanographic parameters other than salinity also changed at the 44°S transition. Nitrate levels were higher in the subantarctic (11–16 μM) and polar ($>20 \mu\text{M}$) surface water compared with the subtropical convergence zone ($<12 \mu\text{M}$), but chlorophyll *a* was lower [Jones *et al.*, 1998].

Both Bates *et al.* [1998b] and Jones *et al.* [1998] report that, as the season progressed, there were substantial increases in concentrations of sea surface DMS over periods of about 1 week in subtropical convergence zone, subantarctic, and polar waters. Bates *et al.* [1998b] report that average atmospheric mixing ratios of DMS over subantarctic waters increased from approximately 80 pptv during the early part of the intensive ACE 1 experiment to approximately 150 pptv for the latter part. These values roughly correspond to atmospheric DMS mixing ratios at altitudes below 0.5 km and latitudes $>44^{\circ}\text{S}$ of 42 pptv (1 σ range, 26–58 pptv) for the November measurements, and 115 pptv (62–170 pptv) for December. The fact that the aircraft mixing ratio averages are lower may be the result of sampling at higher altitudes and of natural spatial variability.

Mean atmospheric DMS mixing ratios of 53 pptv and 120 pptv were measured for November and December, respectively, at Cape Grim from 1988 to 1992 [Ayers *et al.*, 1995]. By comparison, the average aircraft DMS values at altitudes <0.5 km near Cape Grim were 95 pptv for November and 110 pptv for December. Hainsworth *et al.* [1998] report that DMS measurements at Cape Grim during the ACE 1 intensive period were mostly typical of those from previous years. However, DMS concentrations increased quite sharply on November 21, 1995, and were substantially higher than the monthly average on November 23 (Julian Day 331) [Hainsworth *et al.*, 1998], when aircraft samples were collected close to Cape Grim (Figure 1b).

Thus it appears that the atmospheric distribution of methyl nitrate, methyl iodide, and DMS in the MBL during November and December was related to the different water masses found, but exactly what is causing the differences is not clear. It seems reasonable to assume that atmospheric mixing ratios should roughly be controlled by the geographic distribution of the oceanic organisms or other precursors generating these gases. Griffiths *et al.* [this issue] report increasing concentrations of chlorophyll *a* between late November and early-mid December in the subantarctic region, corresponding to the timing of the observed increases in methyl iodide, methyl nitrate, and DMS south of 44°S . They also observed chlorophyll increases in the Cape Grim area during late November, corresponding to increases in atmospheric DMS concentrations measured at the Cape Grim station. However, we have seen earlier that methyl iodide and methyl nitrate can exhibit very different distributions at tropical and subtropical latitudes.

5. Summary and Conclusions

The extensive latitudinal profile sampled by aircraft in early November revealed strong latitudinal gradients for many NMHC and halocarbon gases, including ethane, ethyne, and tetrachloroethene. High mixing ratio enhancements in the northern hemisphere extended up to the maximum altitude of 8 km. These enhancements were the result of the proximity of strong anthropogenic source regions for these gases, principally on the Asian continent. By contrast, methyl chloride exhibited low concentrations in the lower troposphere in the high-latitude northern hemisphere, but significantly elevated levels at midlatitudes, suggesting a high-latitude oceanic sink and a low-latitude Asian source for this gas. Very low mixing ratios were observed in the remote equatorial regions (between about 10°N to 20°S) for all gases except those with oceanic sources. Methyl nitrate appears to have a significant equatorial oceanic source; however, the different distributions of methyl iodide and of methyl nitrate indicate that the two gases have distinct oceanic production mechanisms and/or air-sea exchange processes.

Continental plumes containing material characteristic of biomass burning were observed at mid to high altitudes between approximately 19°S and 43°S. These plumes represented a significant perturbation to the levels of many trace gases, including ozone. They were considerably aged, suggesting that the emissions may have originated from the South Atlantic region.

The 24-day intensive investigation of the remote marine troposphere at midlatitudes south of Hobart revealed a significant increase in average mixing ratios of methyl iodide, methyl nitrate, and DMS in the MBL between late November and early December. This increase was associated with the rapid transition to summer conditions in the region. The region most affected was to the south of 44°S over waters characterized as subantarctic and polar. The onset of summer was also responsible for seasonal decreases in the mixing ratios of ethane, ethyne, propane, and tetrachloroethene.

Acknowledgments. We would like to express our appreciation to the excellent team at UCI who worked so hard in the laboratory, at the computer, and in the field to produce this NMHC and halocarbon data set. They are John Bilicska, Tim Blake, Nancy Conebeare, Kathi Farrow, Michael Gilligan, Adam Hill, Jenn Lapierre, Brent Love, and Murray McEachern. We are also grateful to Barbara Yu for her help during the project and with manuscript preparation, and to Tim Bates and Brian Griffiths for useful discussions. We would like to acknowledge the ACE 1 CO and ozone measurement group, Greg Kok, Andre Prévôt and Dick Schillawski. This research is a contribution to the International Global Atmospheric Chemistry (IGAC) Core Project of the International Geosphere-Biosphere Program (IGBP) and is part of the IGAC Aerosol Characterization Experiments (ACE). Grant ATM-9418773.

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Received September 30, 1998; revised March 1, 1999;
accepted April 2, 1999.